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Synthesis of Linear, Double Chain,
Ladder Polymers from Substituted Tetrachosphonitriles

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ABSTRACT

Thermal polymerization of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$ requires higher temperatures than does the thermal polymerization of $[\phi\text{PN}(\text{NH}_2)]_4$. Because mono, di and trimethylamine and ammonia are eliminated during the polymerization, the resulting product cannot be well characterized.

Attempts to further polymerize low molecular weight polymers of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ have not been successful. It is believed that small amounts of water absorbed by the solid polymer cause partial hydrolysis at higher temperatures which result in depolymerization.

Low molecular weight polymers have been prepared by treating β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, NiCl_2 and CoCl_2 . Thermal deammoniation begins at a lower temperature when CuSO_4 is present. The resulting polymers are of low molecular weight, approximately 3000 - 4000.

Reaction of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with pyromellitic dianhydride in DMF at high temperatures results in the formation of a black insoluble solid. At room temperature a chloroform soluble product is formed that is believed to be a 1:1 condensation compound.

RESULTS AND DISCUSSION

I. Polymerization of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

A. Thermal Polymerization

Thermal polymerization of β -trans- $[\phi\text{PN}(\text{NHMe})]_4$ requires higher temperatures than does the polymerization of the analogous tetraamide. Table I shows results obtained for the thermal deamination of $[\phi\text{PN}(\text{NHMe})]_4$.

TABLE I

Thermal Polymerization of β -trans- $[\phi\text{PN}(\text{NHMe})]_4$

Temp. (°C)	CH_3NH_2 Half-Life	Evolved Yld. Amine	% Prod. Sol. in CHCl_3	Mol. Wt. Prod.	Mol. Wt. Highest cut(s)
305	6	86	100	1,570	8,780
335	2	85	100	1,820	5,150-8,140
375	0.5	80	7%	2,030	-
400	0.3	73	5	690	-
310	3.8	77	90	1,760	11,000
350	0.5	80	25	3,250	17,090-16,000

Polymerizations were carried out by heating the cyclic tetramer under a stream of nitrogen. Evolved gas was passed into water and continually titrated with acid. In this manner the progress of the reaction was followed. After completing the deamination, the residue was taken up in chloroform and fractions precipitated with n-hexane. The first fraction contained the highest molecular weight material.

Several of the lower molecular weight samples were examined by proton NMR spectroscopy. In each case the peak attributed to methyl groups was too broad to distinguish different methyl group environments. The broadness and lack of detail of the methyl absorption persisted after D_2O exchange and P^{31} decoupling. It was noted also that the phenyl proton to methyl proton ratio was too high. In one instance the phenyl proton/methyl proton ratio was 7.1/1. For a high molecular weight polymer, this ratio should approach 3.3/1. The low methyl content of the polymer was confirmed by elemental analysis.

Found: C, 55.26; H, 5.15; N, 15.21; P, 23.14

The empirical formula derived from the above elemental analysis is $\text{C}_{24.6}\text{H}_{27}\text{N}_6\text{P}_4$. If it is assumed that no benzene is lost during polymerization, then the ϕ/CH_3 ratio is 6.6/1.

In order to determine the nature of the deamination products a run was made in which 3.854 g of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$ was heated at 300°C in a stream of dry helium. All volatile products were collected in a liquid nitrogen trap. The reaction was stopped at the end of 5 hours. The weight lost by the sample was 0.68 g; that recovered in the trap was 0.62 g or 92 percent of the volatiles. Results of mass spectral analysis of the volatiles are given in Table II.

TABLE II
Analysis of Thermal Deamination
Products of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

<u>Found</u>	<u>Mole %</u>	<u>g.</u>
methlamine	42.3	0.217
dimethylamine	11.7	0.093
trimethylamine	17.5	0.184
ammonia	24.8	0.074
benzene	3.7	0.052

The remaining polymeric material had a number average molecular weight of 2,000 as determined by VPO in chloroform. Elemental analysis of this material gave the following results.

Found: C, 56.31; H, 4.70 N, 15.71; P, 23.08

Calc'd from Mass Spec.: C, 54.95; N, 14.79

The empirical formula calculated from the analysis is $\text{C}_{24.8}\text{H}_{24.8}\text{N}_{6.4}\text{P}_4$, for which the ϕ/CH_3 ratio is 5.0/1.

Apparently $[\phi\text{PN}(\text{NHCH}_3)]_4$ does not undergo a simple elimination of methylamine during thermal polymerization. The presence of dimethylamine and trimethylamine and ammonia would suggest a rather complex mode of amine elimination leading to products which could not readily be characterized.

B. Polymerization of $[\phi\text{PN}(\text{NHCH}_3)]_4$ in Presence of BF_3

In an attempt to polymerize the tetrakis(methylamide) under milder conditions, the tetramer was treated with BF_3 to form an adduct which upon heating in a suitable solvent might eliminate $\text{CH}_3\text{NH}_2:\text{BF}_3$. The reaction was carried out in chlorobenzene at 100°C for 24 hours, however, upon working up the resultant mixture no evidence was found for the formation of an amine boron trifluoride adduct. The reaction was repeated at 131° with the same negative result. This approach therefore was abandoned.

C. Reaction of $[\phi\text{PN}(\text{NHCH}_3)]_4$ with $[\phi\text{PNCl}]_4$ in Pyridine

In another attempt to prepare a polymer bridged by NCH_3 groups, equimolar amounts of $\beta\text{-trans-}[\phi\text{PN}(\text{NHCH}_3)]_4$ and $\beta\text{-trans-}[\phi\text{PNCl}]_4$ in pyridine was maintained at reflux for 72 hours, after which time the mixture was distilled at reduced pressure. Pyridine hydrochloride was recovered by vacuum sublimation of the residue. Twenty-five percent of the available chlorine was thus recovered as pyridine hydrochloride. The remaining residue was readily taken up in chloroform and fractionally reprecipitated with n-hexane. An infrared spectrum of this material is shown in Figure 1. The number average molecular weight was determined as 1,330 by VPO in CHCl_3 .

Further characterization of this product is now in progress.

II. Polymers of $\beta\text{-trans-}[\phi\text{PN}(\text{NH}_2)]_4$

A. Coupling with $\beta\text{-trans-}[\phi\text{PNCl}]_4$

The possibility of using the largest polymer obtained to date as a prepolymer was investigated. We had hoped to couple ladders with a variety of di- or tetrafunctional molecules and thereby significantly increase the molecular weights.

The first attempt was made by refluxing a polymer sample (mol. wt. 20,900) with a stoichiometrically equivalent amount of $\beta\text{-trans-}[\phi\text{PNCl}]_4$ in methylene chloride. The mixture was held at reflux for 24 hours. After working up the mixture a sample of amide polymer was recovered that had a molecular weight of 1,320. A similar result was obtained when the reaction was repeated, however, the phosphonitrile amide polymer now had a molecular weight of 3,380. Infrared spectra for the starting material and the final product are shown in Figures 2 and 3 respectively. Positive identification of the strong absorption peak at 1650 cm^{-1} has not been made; however, interaction of the solvent with the polymer may have led to the formation of $-\text{N}=\text{CH}_2$ bonds which would account for the observed spectrum.

The unexpected depolymerization led to a study of the stability characteristics of the polymer.

B. Stability Studies of $\beta\text{-trans-}[\phi\text{PN}(\text{NH}_2)]_4$ Polymers

Polymer resulting from the thermal deammoniation of $\beta\text{-trans-}[\phi\text{PN}(\text{NH}_2)]_4$ was refluxed in both anhydrous methylene chloride and reagent grade chloroform. Molecular weights were then determined for the polymer. Results are summarized in Table III, also included are the two runs discussed in the previous section.

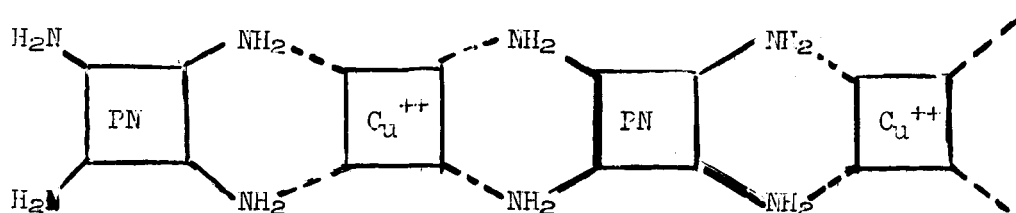
TABLE III
Depolymerization of Tetraamide Polymer

Initial Polymer (Mol. Wt.)	Reagent	Duration of Test	Final Polymer (Mol. Wt.)
20,900	CCl ₄	6 Hrs.	13,100
20,900	CCl ₄	22 Hrs.	10,200
20,900	CH ₂ Cl ₂	24 Hrs.	15,400
20,900	CH ₂ Cl ₂ + β -Trans-[\emptyset PNCl] ₄	24 Hrs.	1,320
20,900	CH ₂ Cl ₂ + β -Trans-[\emptyset PNCl] ₄	24 Hrs.	3,380

In another experiment, polymer of 20,900 molecular weight was heated in absence of solvent at 300° in a stream of dry nitrogen. The resulting ammonia evolution was in excess of -NH₂ groups calculated to be present. The residue, after heating, had a molecular weight which was lower than the starting material. This experiment was repeated at 265°C with the same results. No clue as to the cause of degradation was observed in the IR spectrum of the degraded polymer. It is probable that the cause of degradation in all of these experiments is hydrolysis as caused by trace amounts of water. The latter runs, carried out in the absence of any solvent, serves to pinpoint the source of the water to the polymer itself. Presumably the polymer can absorb enough water to lead to depolymerization upon heating. This would account for the excessive evolution of ammonia when the polymer, containing only a small number of NH₂ groups, is reheated at 300°C.

III. Polymerization of β -trans-[\emptyset PN(NH₂)]₄ in the Presence of Transition Metal Salts.

Preparation of inorganic polymers via coordination with metals is well known. However, there is essentially no literature on the coordination of metals with phosphonitriles. We have undertaken an investigation of the polymerization of β -trans-[\emptyset PN(NH₂)]₄ in the presence of transition metals that tend to coordinate strongly with amines. Such complexes or polymers may serve two purposes. First, the stereospecificity of the complex may favor the formation of ladder type polymers; for example, the polymer resulting from Cu⁺⁺, which forms square planar complexes, can be envisioned as follows.



Secondly, transition metal salts, acting as Lewis acids, may catalyze the elimination of ammonia so that thermal polymerizations could be carried out at lower temperatures.

The ability of such cations as Cu^{++} , Ni^{++} , Co^{++} and Ag^+ to form complexes with β -trans- $[\text{OPN}(\text{NH}_2)]_4$ was examined. From these metal ions square planar, octahedral, or linear complexes can be formed.

Several reactions of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ with β -trans- $[\text{OPN}(\text{NH}_2)]_4$ were carried out in solution and in a melt. From a reaction carried out in chlorobenzene at 90°C for 2 days, 90 percent of the starting material was recovered. However, a small amount of chloroform soluble light green solid also was recovered. The infrared spectrum, Figure 4, indicates that this material does contain the P-N ring. In another experiment, for which the solvent consisted of water and chlorobenzene, the mixture of CuSO_4 (in water) and the tetraamide (in chlorobenzene) were stirred for seven days. During this time a solid formed at the interface but was lost during the subsequent work-up.

Reactions carried out in the absence of solvent produced low molecular weight polymers. A mixture of the tetraamide and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in a ratio of 1:4 was heated at 200 - 220° for 16 hours. The crude product was extracted with chloroform and a polymer of 4,720 average MW was recovered. An infrared spectrum of the polymer is shown in Figure 5. The strong absorption at 900 cm^{-1} is typical of many of the polymers derived from the tetraamide. The elemental analysis, given below, indicates that there is approximately one Cu^{++} per five tetramer units.

Found: C, 51.79; H, 4.14; N, 12.64 P, 21.72; Cu, 2.12.

Because the analysis does not add up to 100 percent, when sulfate and H_2O are included, the product may have been partially hydrolyzed.

The above melt reaction was repeated with tetraamide and $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in a mole ratio of 1:2.5. The mixture was kept at 240°C for six hours. The soluble polymeric product isolated by extraction with chloroform had a number average molecular weight of 3600. The elemental analysis was as follows.

Found: C, 50.16; H, 3.81; N, 11.63; P, 21.57; Cu, 5.02.

According to this analysis there are two tetrameric units per Cu^{++} , however, the nitrogen analysis is somewhat low.

In another reaction of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ with the tetraamide (10:1 mole ratio) ammonia evolution was first noted at 180° , almost 30° lower than the thermally induced polymerization. After six days at 200°C only 37 percent of the ammonia expected for complete deammoniation was evolved. If the water present as the monohydrate had caused hydrolysis resulting in the evolution of ammonia, then a greater amount of NH_3 should have been eliminated. The polymer resulting from this reaction was completely insoluble in chloroform.

Complexes or polymers have also been prepared by heating β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with CoCl_2 and NiCl_2 . From both reactions a chloroform soluble product was obtained. Infrared spectra for these products are similar to those of the copper complexes.

The reaction of tetraamide with AgCl in the melt results in the formation of an insoluble product.

These reactions do imply that the metals are incorporated in the polymer. Further work on preparation of these complexes or polymers in such solvents as THF or acetonitrile are now underway.

IV. Reactions of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

A. Reaction with Pyromellitic Tetraacid Chloride (PMTCl)

The reaction of $[\phi\text{PN}(\text{NH}_2)]_4$ with PMTCl in pyridine was reported in the Second Quarterly Report. The only product isolated from this reaction analyzed very well for $[\phi\text{PN}(\text{NH}_2)]_4 \cdot 3\text{HCl}$.

Found: C, 43.45; H, 4.82; N, $\begin{cases} 17.08 \\ 16.90 \end{cases}$; P, $\begin{cases} 18.74 \\ 18.55 \end{cases}$; Cl, 15.88.

Calc'd for: $\text{C}_{24}\text{H}_{31}\text{N}_8\text{P}_4\text{Cl}_3$: C, 43.60; H, 4.73; N, 16.45; P, 18.72; Cl, 16.08.

No polymeric product containing the pyromellitic acid group was isolated.

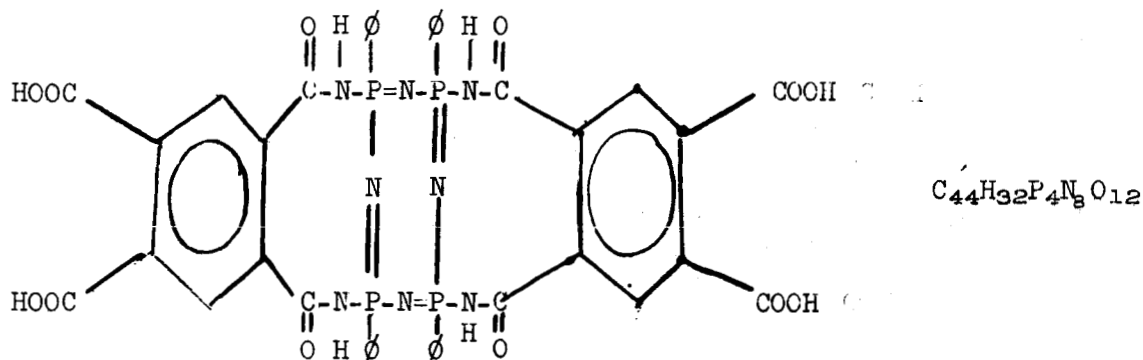
B. Reaction with Pyromellitic Dianhydride (PMDA)

Four reactions were carried out in which an equimolar amount of PMDA was reacted with the tetraamide in DMF. The first reaction, reported previously, resulted in the isolation of a material which had a molecular weight of approximately 1,400.

In an effort to prepare polymers of higher molecular weight, two reactions were carried out at reflux wherein one reagent was slowly added to the other. Water, formed as a byproduct, was continually removed by distillation. In both cases, a black insoluble resinous solid remained after vacuum distillation of the DMF. The solids are not readily soluble in common organic solvents and appear to be somewhat hygroscopic. Elemental analyses of both materials are as follows:

Found: A: C, 49.19; H, 4.82; N, 11.48; P, 12.86; $[\text{O}]$ 21.65 diff.
B: C, 51.70; H, 5.44; N, 11.4; P, 12.35; $[\text{O}]$ 19.11 diff.

Empirical formulae for both materials are: for (A) $\text{C}_{40}\text{H}_{46.8}\text{P}_4\text{N}_8\text{O}_{12}$; for (B), $\text{C}_{42.8}\text{H}_{54}\text{P}_4\text{N}_8\text{O}_{12}$; which can be approximated by the following unit.



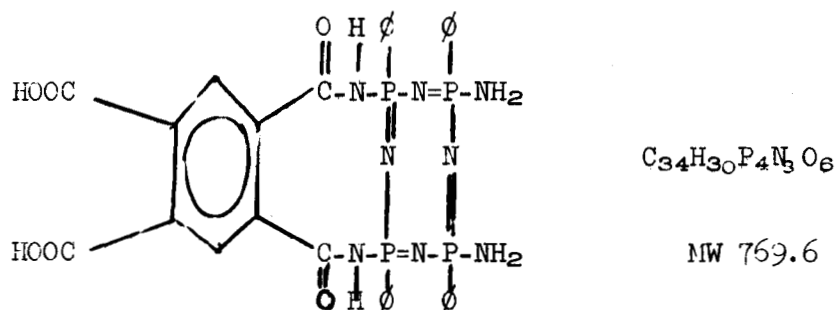
From the reaction of PMDA with the tetraamide in DMF at room temperature was obtained a light tan solid, in contrast to those described above, that was partially soluble in chloroform. The chloroform insoluble solid analyzed as follows:

Found: C, 48.19; H, 4.64; N, 12.44; P, 12.43; O, 22.3 (diff.)

Based on this analysis, the empirical formula is $C_{40}H_{46}P_4N_8O_{14}$. The chloroform soluble fraction, however, analyzed as follows:

Found: C, 52.65; H, 5.47; N, 12.28; P, 17.44; [O], 12.16 (diff.)

The empirical formula is $C_{31.3}H_{38.04}N_{6.2}P_4O_{5.4}$. An infrared spectrum of this material is shown in Figure 6. The molecular weight, determined by VPO in chloroform, was 830. The soluble reaction product may be primarily the following



It can be concluded that the reaction of PMDA with tetraamide results in the formation of very low molecular weight polymers that are relatively insoluble and difficult to characterize.

C. Attempted Preparation of $[\phi\text{PN}(\text{NCO})]_4$

Initial attempts to prepare β -trans- $[\phi\text{PN}(\text{NCO})]_4$ by reacting $[\phi\text{PN}(\text{NH}_2)]_4$ with phosgene was reported in the Second Quarterly Report. Elemental and infrared analysis of the product suggested that coupling had taken place to form a low molecular weight polymer with -NHCONH- bridges.

The reaction of phosgene with the tetraamide was repeated several times under different conditions. In each case the product appeared to be a low molecular weight polymer. In no case was an isocyanate isolated. We do not plan any further work on the preparation of this derivative.

D. Reaction of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with Formaldehyde

In an attempt to prepare a monomer that would undergo low temperature polymerization reactions, β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ was treated with formaldehyde. The expected reaction to form the methylol derivative is given by the following equation.



The reaction was carried out in methanol at reflux using aqueous formaldehyde. A material isolated from the reaction products gave the following elemental analysis.

Found: C, 54.69; H, 6.18; N, 15.32; P, 16.97; [O], 6.84.

An empirical formula, based on the above analysis, is $\text{C}_{33.3}\text{H}_{45.2}\text{P}_4\text{N}_{7.96}\text{O}_{3.12}$. From the analysis it is believed that the product contains -NHCH₂OCH₃ groups. The strong absorption band at about 1060 cm.⁻¹ in the infrared spectrum (Figure 7) may be attributed to -C-O-C-.

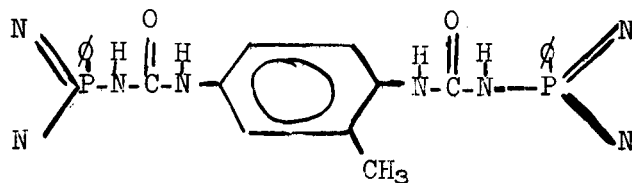
The reaction was repeated using paraformaldehyde as a source of anhydrous formaldehyde. The reaction was carried out in anhydrous methanol. The product recovered from this reaction analyzed similarly to that of the first reaction.

Found: C, 54.39; H, 6.01; N, 14.73; P, 16.15; [O], 8.72.

The calculated empirical formula is $\text{C}_{34.8}\text{H}_{45.7}\text{P}_4\text{N}_8\text{O}_4$.

E. Reaction of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ with Toluene-2, 4-Diisocyanate

The condensation of amines with diisocyanates is well known. We have attempted the polymerization of $[\phi\text{PN}(\text{NH}_2)]_4$ with toluene -2, 4-diisocyanate in an attempt to form the following type of bridging groups.



Upon addition of two equivalents of toluene diisocyanate to the tetraamide in xylene a precipitate formed which, upon separation, had the following elemental analysis.

Found: C, 56.40; H, 4.76 N, 18.84; P, 10.70; [O], 9.30 (diff.).
for $C_{15}H_{15}N_5PO_2$: C, 54.85; H, 4.62; N, 21.35; P, 9.42; O, 9.78.

This material does not melt at $300^{\circ}C$. Molecular weights could not be determined because of its insolubility in a variety of organic solvents. From the elemental analysis, however, the most likely unit structure is the one shown above.

EXPERIMENTAL

I. A. Thermal Polymerization of β -trans- $[\phi\text{PN}(\text{NHCH}_3)]_4$

The method used to thermally polymerize the tetrakismonomethylamide was described in the previous Quarterly Report. Briefly, a 3.0 g sample of the material was heated in a furnace under a nitrogen stream. The effluent gas was passed into water where evolved amine was titrated with standard acid.

B. Attempted Polymerization of $[\phi\text{PN}(\text{NHCH}_3)]_4$ in the Presence of BF_3

Two grams (3.29 mmoles) of $[\phi\text{PN}(\text{NHCH}_3)]_4$ and 6.58 mmoles of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in chlorobenzene was kept at 100°C for 24 hours. Only a slight haziness developed during this time. Upon evaporation of the solvent only starting material was recovered.

The reaction was repeated at 131°C with the same results.

C. Reaction of $[\phi\text{PN}(\text{NHCH}_3)]_4$ with $[\phi\text{PNCl}]_4$ in Pyridine

In 50 ml of anhydrous pyridine 3 g (4.93 mmoles) of $[\phi\text{PN}(\text{NHCH}_3)]_4$ and 2.62 g (4.93 mmoles) of $[\phi\text{PNCl}]_4$ were dissolved and the solution brought up to reflux at 115°C . After 72 hours the solvent was removed by distillation at reduced pressure. The residue was then transferred to a sublimation apparatus and at 175° and 0.010 Torr a sublimate was collected. The sublimate was dissolved in water and analyzed for chloride. Five mmoles of chloride were found as AgCl .

The remaining residue was taken up in 10 ml of chloroform and upon addition of pentane an oil separated which, when triturated, turned to a solid. Molecular weight of this solid is 1,330 as determined by VPO in chloroform.

II. Polymers of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

A. Attempted Coupling with β -trans- $[\phi\text{PNCl}]_4$

In 20 ml of anhydrous methylene chloride 0.3090 g (0.0148 mmole) of amide polymer of molecular weight 20,900 and 0.0093 g of $[\phi\text{PNCl}]_4$ was refluxed at 39°C in a nitrogen sweep for 24 hours. During this time no ammonia evolution was noted. The solvent was evaporated and the residue taken up in chloroform. A molecular weight of 1,320 was determined by VPO. If there were no interaction the measured average molecular weight should have been approximately 10,000.

B. Stability Studies of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$

Samples of tetraamide polymers, 20,900 MW, were refluxed in chloroform and methylene chloride, after which the solvent was removed by distillation. Molecular weights of the residue were then determined by VPO in chloroform. Results are given in Table III.

III. Polymerization of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ in the Presence of Transition Metal Salts

A. Reaction with Cu^{++}

1. In Chlorobenzene

Copper sulfate monohydrate was obtained by heating $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ for five hours at 110°C . To a solution of 100 ml of chlorobenzene and 2.0 g (3.6 mmoles) of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ was added 1.3 g (7.2 mmoles) of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. The mixture was kept at 90°C for 48 hours. The chlorobenzene solution developed a bright green color during this time.

After filtering the inorganic salts, from the filtrate was recovered 1.8 g of unreacted tetramer and approximately 0.2 g of a light green solid that was soluble in chloroform. The infrared spectrum is shown in Figure 4.

2. In Chlorobenzene - Water

A two-phase reaction was conducted with 3.7 mmoles of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ in 100 ml of chlorobenzene and 3.4 mmoles of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 ml of water. The two-phase mixture was stirred for one week at $90 - 95^\circ\text{C}$. During this period the organic layer developed a green color and a fibrous material appeared at the interface. This material was soluble in chloroform but was destroyed by excessive heating while attempting a purification.

3. Melt Reactions

One gram (1.8 mmoles) of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ was intimately mixed with 1.82 g (10.3 mmoles) of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ and heated to 200°C . The mixture was maintained at $200-220^\circ\text{C}$ for sixteen hours after which it was washed with chloroform. The light green solid isolated from the chloroform, 0.79 g, had a molecular weight of 4720 as determined by VPO.

The melt reaction was repeated using 3.0 g (5.4 mmoles) of tetraamide and 1.82 g (2.2 mmoles) of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. The mixture was kept at 240°C for six hours. Chloroform soluble product recovered from this reaction had a molecular weight of 3600.

In a third reaction 3.0 g (5.4 mmoles) of the tetraamide and 9.63 g (54.5 mmoles) of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ were heated to 200°C . A nitrogen sweep over the mixture was passed into water and titrated with standard acid. Ammonia evolution was first observed at 180°C . After six days at 200°C only 4.04 mmoles of NH_3 was measured. The product obtained from this reaction mixture was insoluble in chloroform.

B. Reaction with Co^{++}

Anhydrous CoCl_2 was prepared by heating $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ for six hours at 130° in an HCl atmosphere. A mixture of 1.5 g (2.7 mmoles) of tetraamide and 0.38 g (2.9 mmoles) of CoCl_2 was heated for seven hours at $210\text{--}240^\circ\text{C}$. The ammonia evolved, 4.0 mmoles, was measured by titration with standard acid. By extraction with CHCl_3 , 1.4 g of a blue solid was isolated. Elemental analysis is as follows:

Found: C, 50.82; H, 4.22; N, 12.76; P, 21.46; Cl, 3.23.

C. Reaction with Ag^+

In a reaction tube, 1.5 g (2.7 mmoles) of tetraamide and 0.8 g (5.4 mmoles) of AgCl were mixed and heated at 230°C for seven hours. During this time 3.7 mmoles of NH_3 was evolved. The grey solid that was formed was insoluble in chloroform and other common solvents. Elemental analysis gave the following results.

Found: C, 22.77; H, 2.05; N, 7.63; P, 12.05; Cl, 12.09.
No further characterization was made.

D. Reaction with Ni^{++}

Two grams (3.6 mmoles) of tetraamide and NiCl_2 (0.46 g, 3.6 mmoles) were mixed intimately and heated at 230°C for ten hours. During this period, 4.1 mmoles of NH_3 was evolved. A gold colored chloroform soluble product was recovered. Elemental analysis gave the following:
C, 53.39; H, 4.43; N, 12.85; P, 21.79; Cl, 2.48.

IV. Reactions of $\beta\text{-trans-}[\phi\text{PN}(\text{NH}_2)]_4$

A. Reaction with PMDA

In each of the reactions carried out 2.0 g of tetraamide was treated with an equivalent amount of PMDA. Reactions at the reflux temperature of DMF were conducted by slowly adding one of the reagents to the other while distilling off a mixture of by-produced water and DMF. After refluxing for several hours solutions were filtered and the filtrate evaporated to dryness at reduced pressure. The black residue obtained in this way was insoluble in all organic solvents tried.

For the reaction carried out at room temperature no attempt was made to remove the water that formed. Contrary to the previous experiments the solution did not turn deep brown. Upon evaporation of DMF at reduced pressure a solid was obtained. The solid was only partially soluble in chloroform. Elemental analyses are given in the Discussion Section.

B. Reaction with Formaldehyde

In methanol, 3.6 mmoles of $[\phi\text{PN}(\text{NH}_2)]_4$ was treated with an excess of aqueous formaldehyde in the presence of two drops of pyridine. The mixture was refluxed for 48 hours during which time a precipitate formed. The precipitate, 1.0 g was recovered by filtration. An infrared spectrum is shown in Figure 7.

C. Reaction with Toluene-2,4-Diisocyanate

To two grams of the tetraamide in xylene was added 2 molar equivalents of the diisocyanate. A precipitate formed during the addition which, after filtration, proved to be an insoluble solid that did not melt at 300°C . No other product was recovered from this reaction.

MANPOWER EXPENDED

The following breakdown shows the cumulative man hours expended to date:

	T h r o u g h		
	<u>December</u>	<u>January</u>	<u>February</u>
Principal Investigator	150	171	201
Department Director	54	64	76
Senior Chemist	1136	1372	1678
Technician	1664	1792	2032
Analytical Chemist	4	25	45
Analytical Technician	6	17	20

PROGRAM PLANNING CHART

Attached is the current planning chart. Dark areas represent work accomplished.

ANTICIPATED WORK

Products of the reaction of $[\phi\text{PN}(\text{NHCH}_3)]_4$ with $[\phi\text{PNCl}]_4$ will be studied.

Reactions of $[\phi\text{PN}(\text{NH}_2)]_4$ and heavy metals will be studied as a means of preparing ladder type polymers.

The chloroform soluble product, resulting from the reaction of PMDA with the tetraamide, will be used to prepare higher molecular weight polymers.

DURATION OF SUBPROJECT

Sub-Project	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	April	May	Professional	Technician	Total
Polymers From $[\text{MePnCl}]_4$													4	6	10
Isolation of $[\text{MePnCl}]_4$													3	4	7
Polymers from $[\text{MePnCl}]_4$													3	4	7
Thermal Studies of $[\text{R}_2\text{Pn}]_4$													3	4	7
	1	2	3	4	5	6	7	8	9	10	11	12	13	18	31

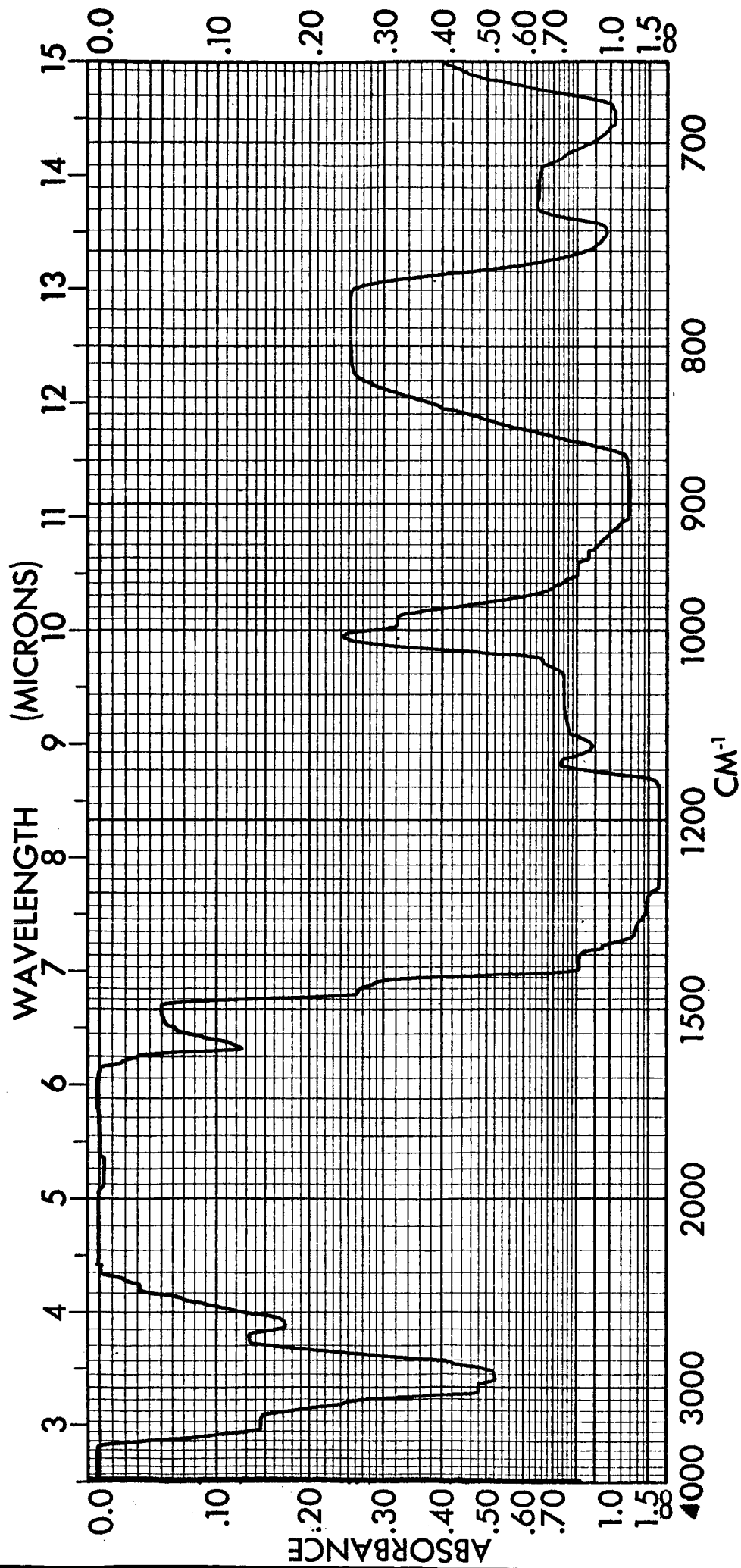


Figure 1

Infrared Spectrum of Product from β -trans-[ϕ PN(NH_2)]₄ and β -trans-[ϕ PNCl]₄

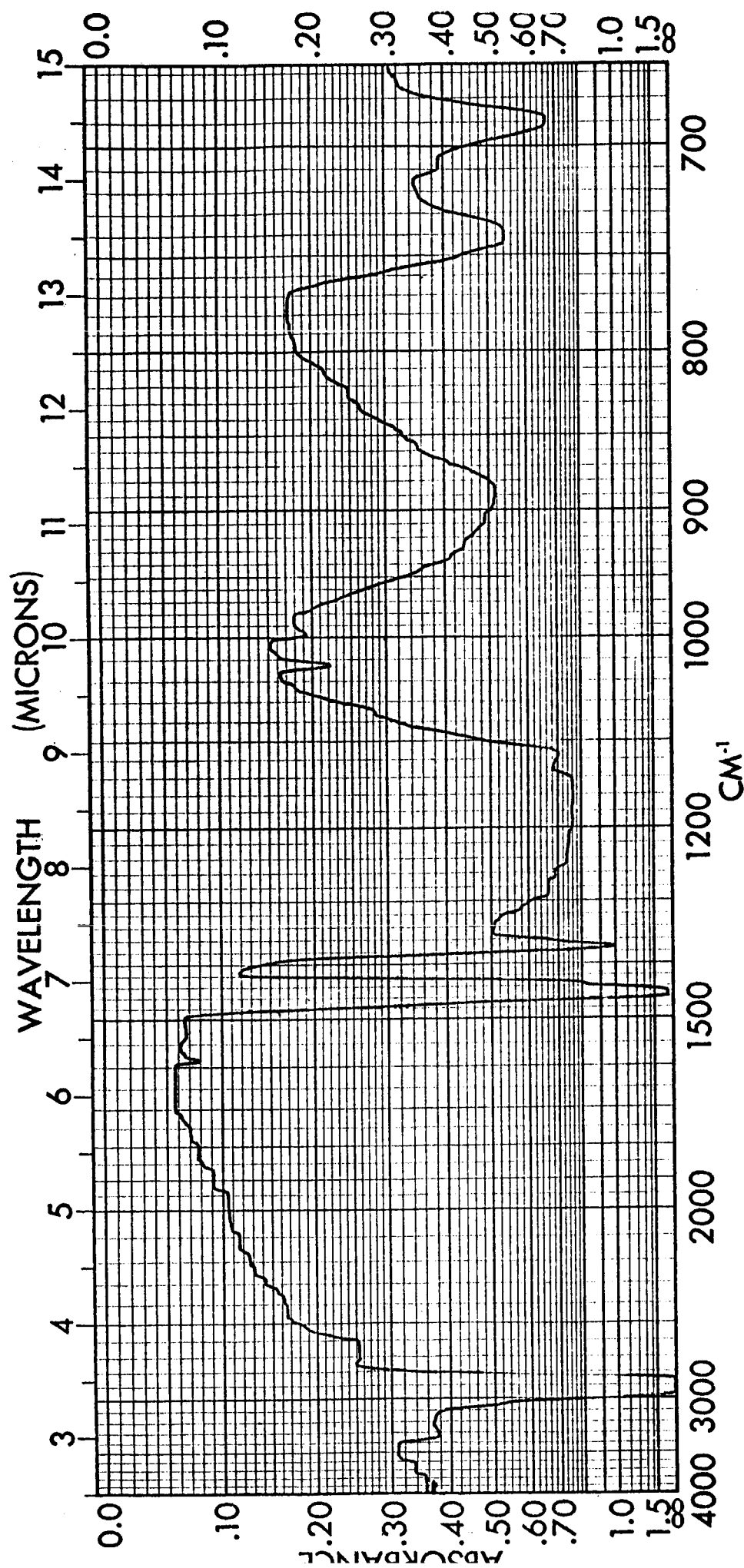


Figure 2

Infrared Spectrum of Polymer from β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ (Mol. Wt. 20,900)

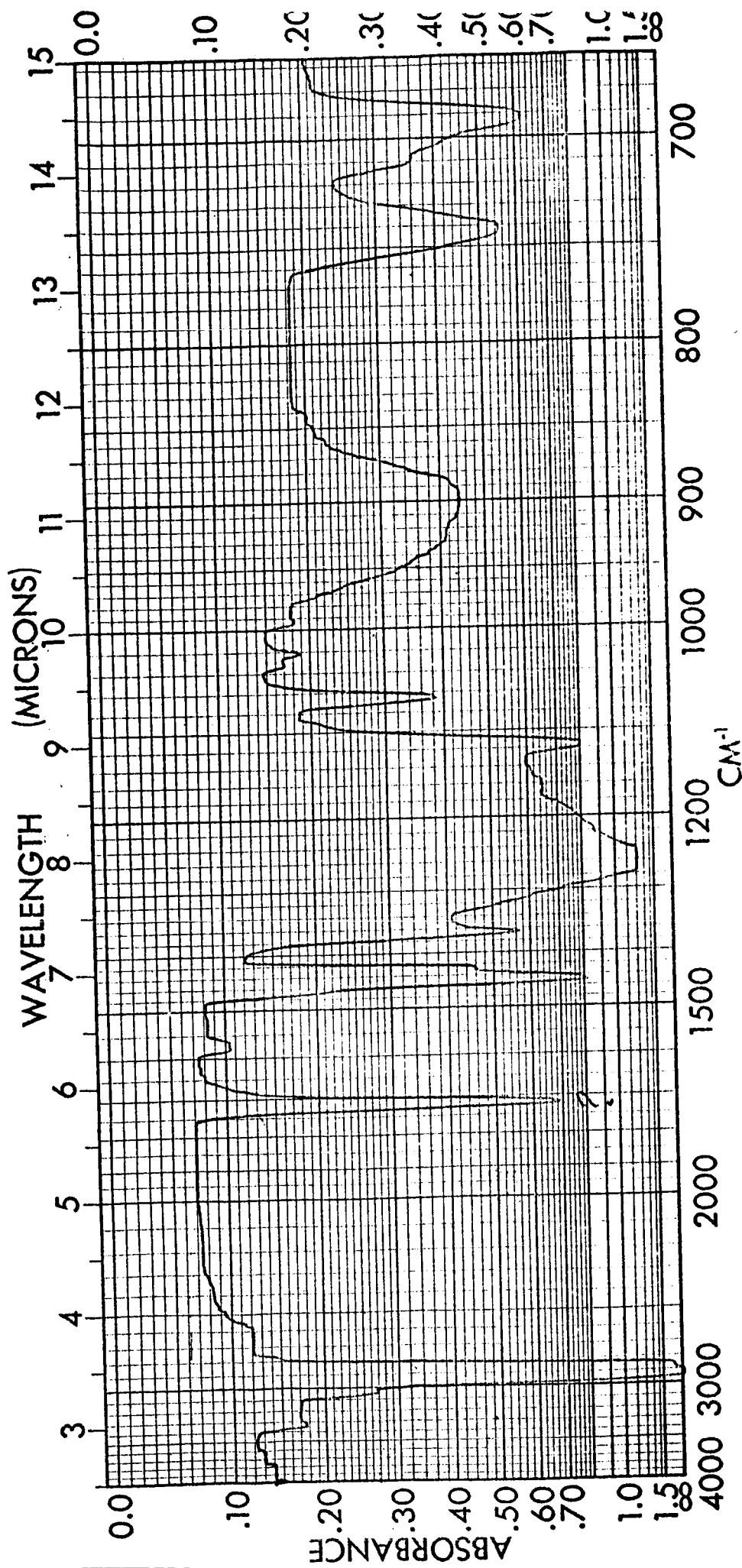


Figure 3

Infrared Spectrum of Polymer from β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ after Depolymerization (Mol. wt. 1300)

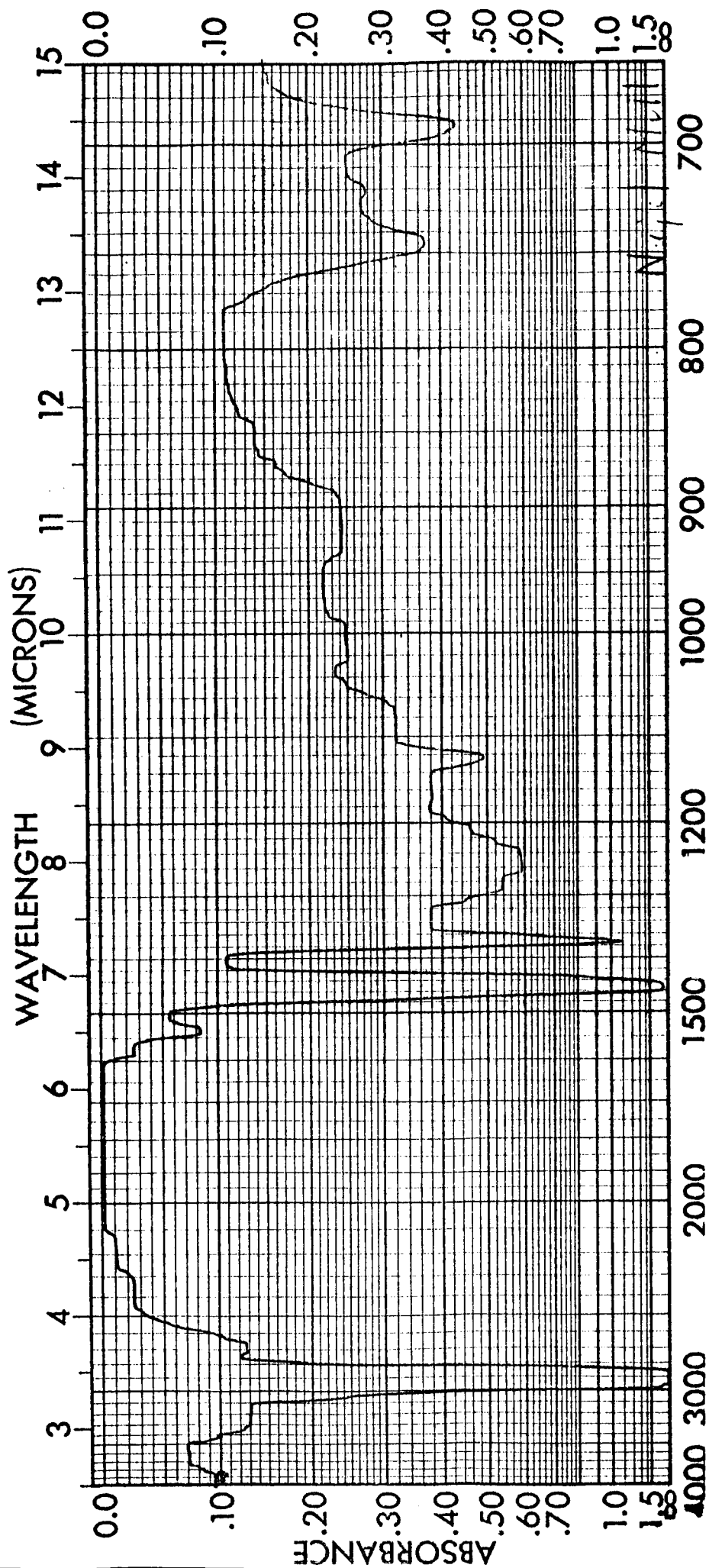


Figure 4

Infrared Spectrum of Product of β -trans- $[\phi\text{PN}(\text{NH}_2)]_4 + \text{C}_u^{++}$ in Chlorobenzene

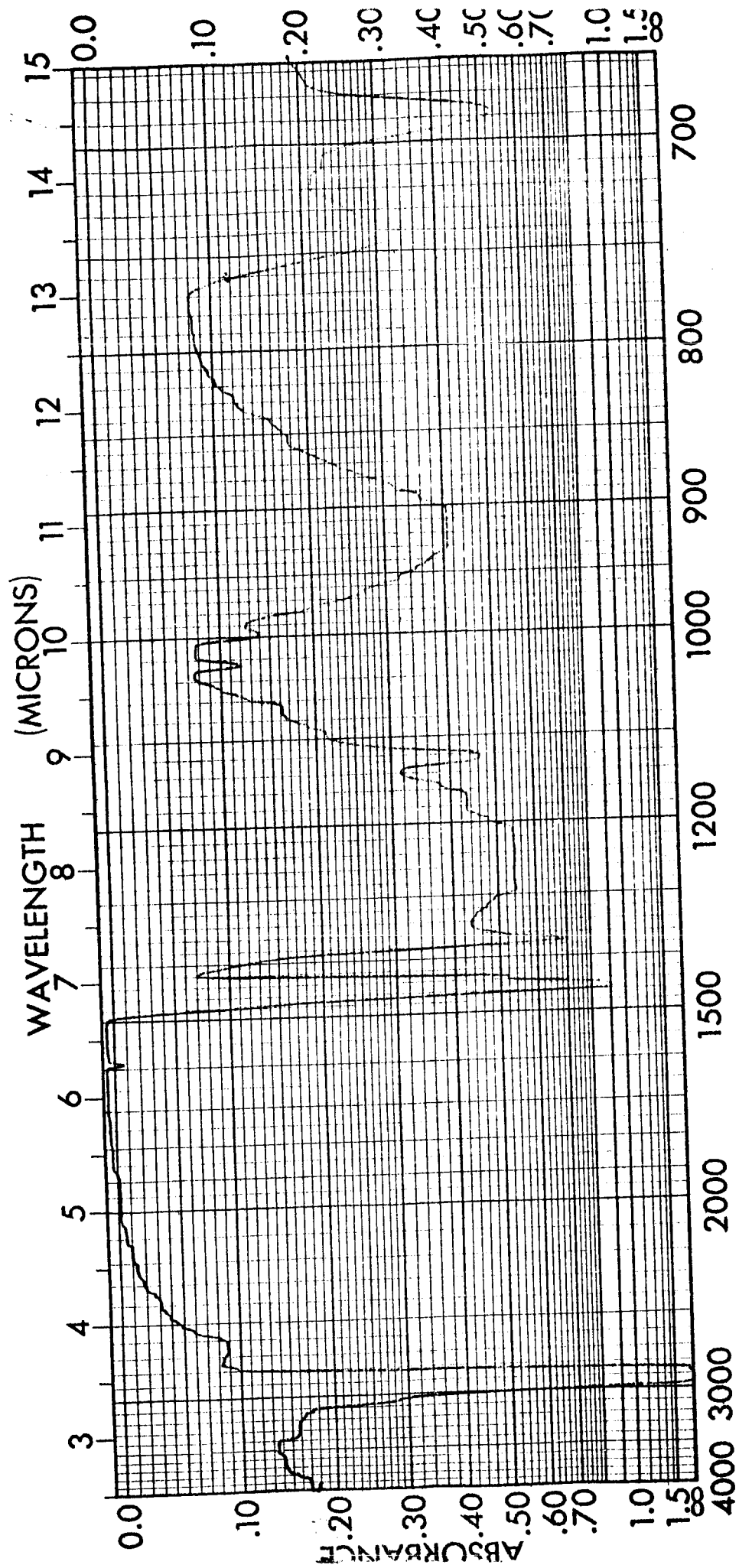


Figure 5

Infrared Spectrum of Product β -trans-[ϕ PN(NH₂)]₄ + Cu⁺⁺ in Melt Reaction

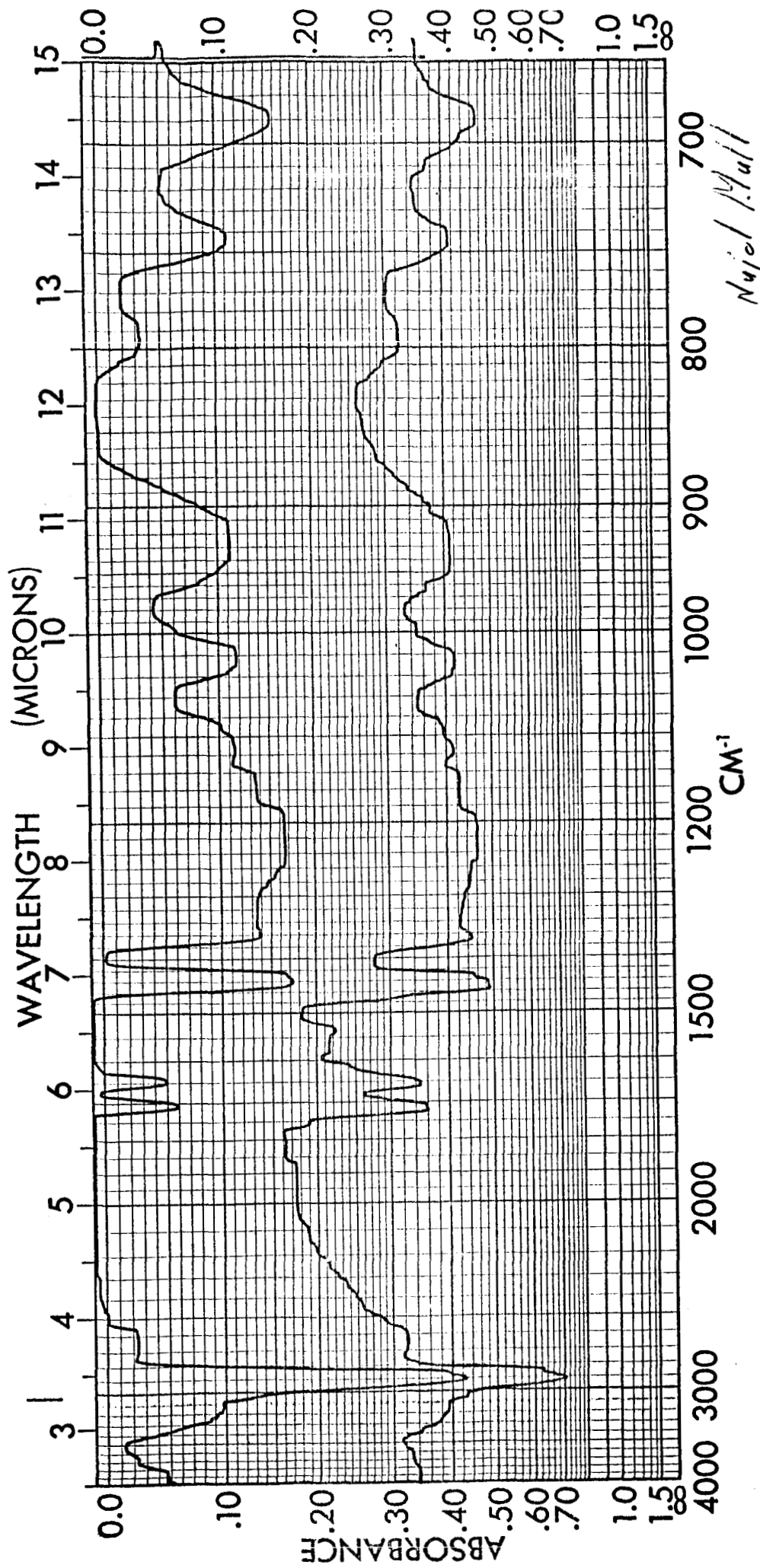


Figure 6

Infrared Spectrum of Chloroform Soluble Product from the Reaction of

β -trans- $[\phi\text{PN}(\text{NH}_2)]_4$ and Pyromellitic Dianhydride in DMF

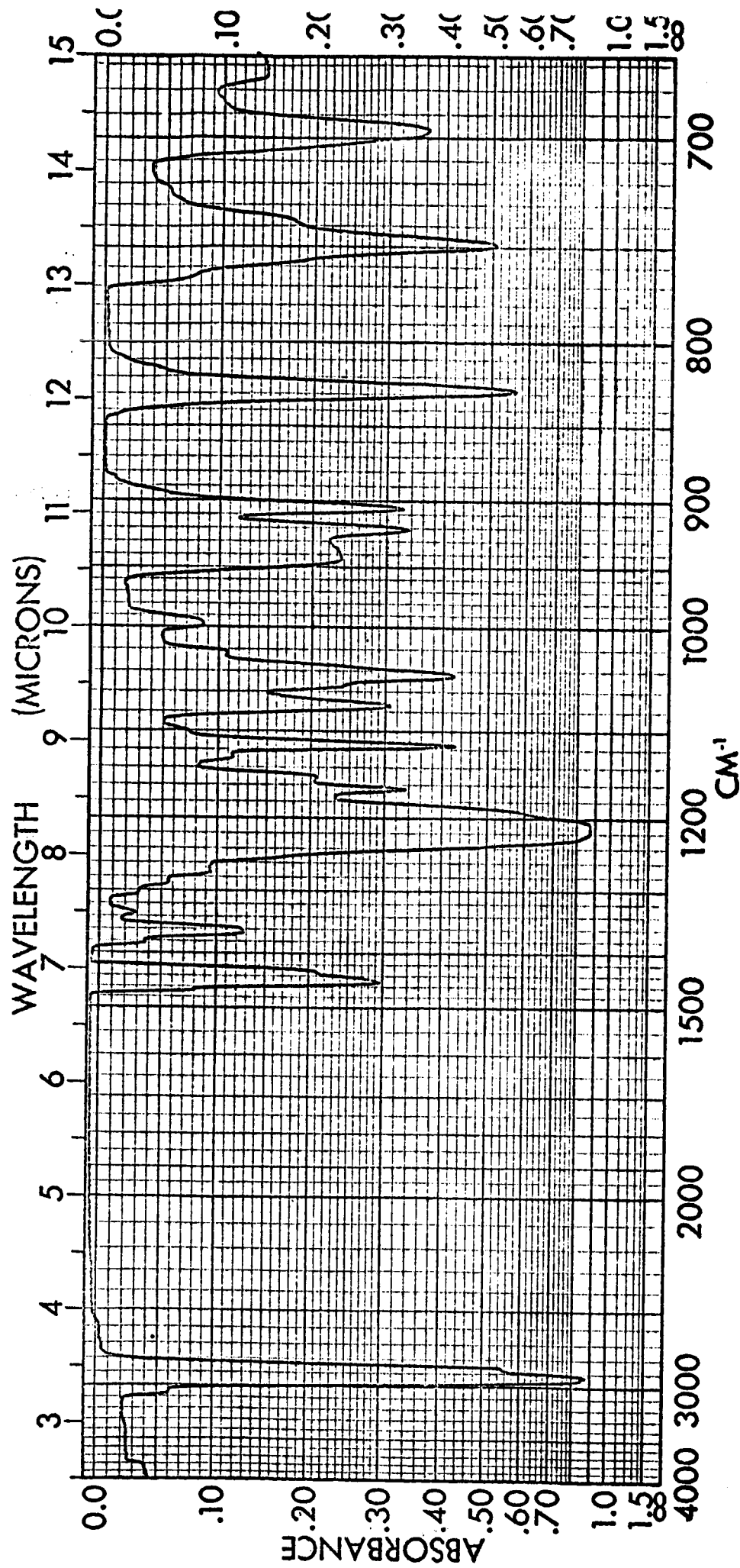


Figure 7

Infrared Spectrum of Product $[\phi\text{PN}(\text{NH}_2)]_4 + \text{H}_2\text{CO}$ in CH_3OH